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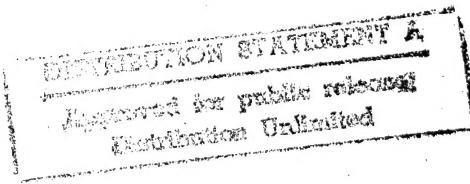
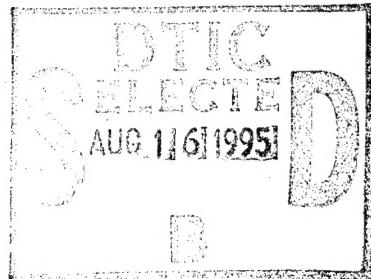
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UNITED STATES ATOMIC ENERGY COMMISSION

THE DETERMINATION OF VANADIUM IN THE  
PRESENCE OF PLUTONIUM

By  
Maynard E. Smith



August 1, 1951

Los Alamos Scientific Laboratory  
Los Alamos, New Mexico



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CHEMISTRY AND METALLURGY DIVISION

ANALYTICAL GROUP

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ABSTRACT

A polarographic method for the determination of vanadium in the presence of plutonium has been devised which does not require a separation of the plutonium. Hydrochloric acid solutions containing both plutonium and vanadium are treated with zinc and zinc amalgam prior to analysis in order to reduce both metals. The plutonium is reduced to the (III) state and the vanadium chiefly to the (II) state. The height of the anodic wave produced by the oxidation of the vanadium is proportional to the total vanadium concentration. Plutonium(III) does not produce an interfering wave. Solutions of V/Pu weight ratio as low as  $6.4 \times 10^{-4}$  may be analyzed by this method with a reproducibility of 3.4% for the 95% level.

## INTRODUCTION

The existence of an anodic wave in dilute acid solutions of vanadium(II) was reported by Lingane in 1945<sup>(1)</sup>. He also reported that at the dropping electrode in dilute acid solutions vanadium(III) was reduced reversibly to vanadium(II), and that the latter is oxidized reversibly to vanadium(III). When a hydrochloric acid solution containing vanadium(II) is analyzed polarographically an anodic wave is produced with a half wave potential of approximately -0.5 volts vs. S.C.E. When zinc was used to reduce hydrochloric acid solutions of plutonium and vanadium and the solutions kept in contact with liquid zinc amalgam until just before analysis, the plutonium was reduced to the non-interfering (III) state<sup>(2)</sup> and on analysis the anodic vanadium(II) wave was formed. This is shown in Figure 1 which is a typical polarogram of a reduced plutonium-vanadium solution taken with the Leeds and Northrup Electro-Chemograph Type E. It was found that under the proper conditions the total height of the wave (measuring peak currents) between -0.3 and -0.7 volts was proportional to the total vanadium concentration. If the reduced solutions were not kept in contact with the zinc amalgam until just before analysis, the cathodic portion of the wave increased (probably due to the formation of vanadium(III)). A similar phenomenon was observed by Lingane<sup>(1)</sup> who suggests that the formation of the vanadium(III) is probably due to the reduction of the hydrogen ion by vanadium(II) or to the oxidation of vanadium(II) by oxygen present in

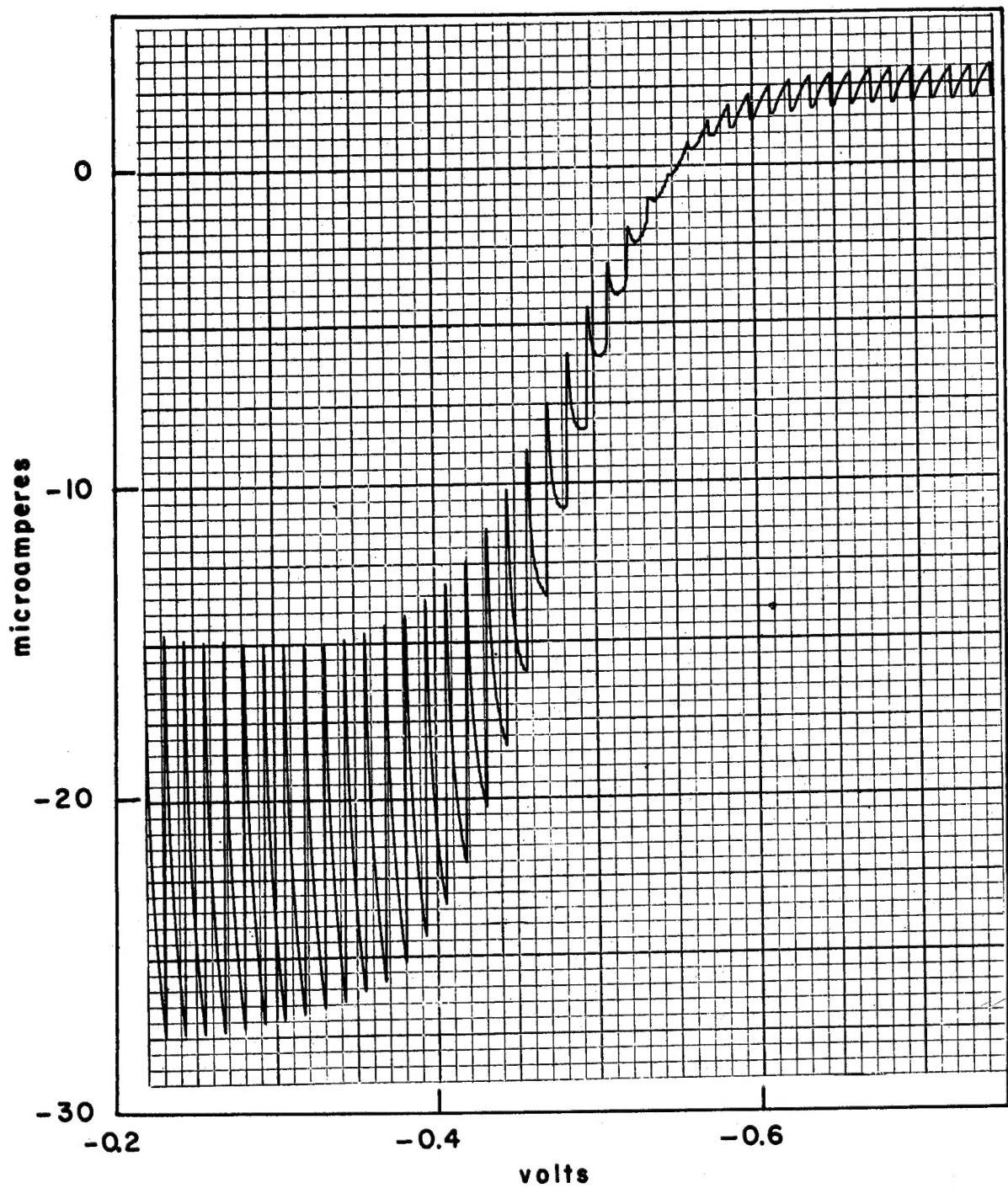


Fig. I HCl solution containing 2 mg V and 60 mg Pu  
reduced with zinc and zinc amalgam.

the nitrogen bubbled through the cell solution.

Since this vanadium anodic wave in the plutonium(III) solutions was well defined and proportional to the vanadium concentration, the method seemed to be feasible for the analysis of small amounts of vanadium in the presence of plutonium.

It could probably also be used for the determination of vanadium in iron, however, in this case electrolytic separation of the iron is quite easily and effectively accomplished<sup>(3)</sup>.

This method cannot be used for the determination of vanadium in uranium due to the interfering anodic wave produced by the oxidation of the uranium(III).

#### APPARATUS AND TECHNIQUE

##### Caution

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

The instrument used for recording the polarograms was a Leeds and Northrup Electro-Chemograph Type E (Figure 2). This is an automatic recording machine using a Speedomax Recorder. Although three degrees of damping are available with this machine, undamped polarograms were used and the curve envelope (maximum current) measured rather than the average current. The advantage of this technique has been pointed out

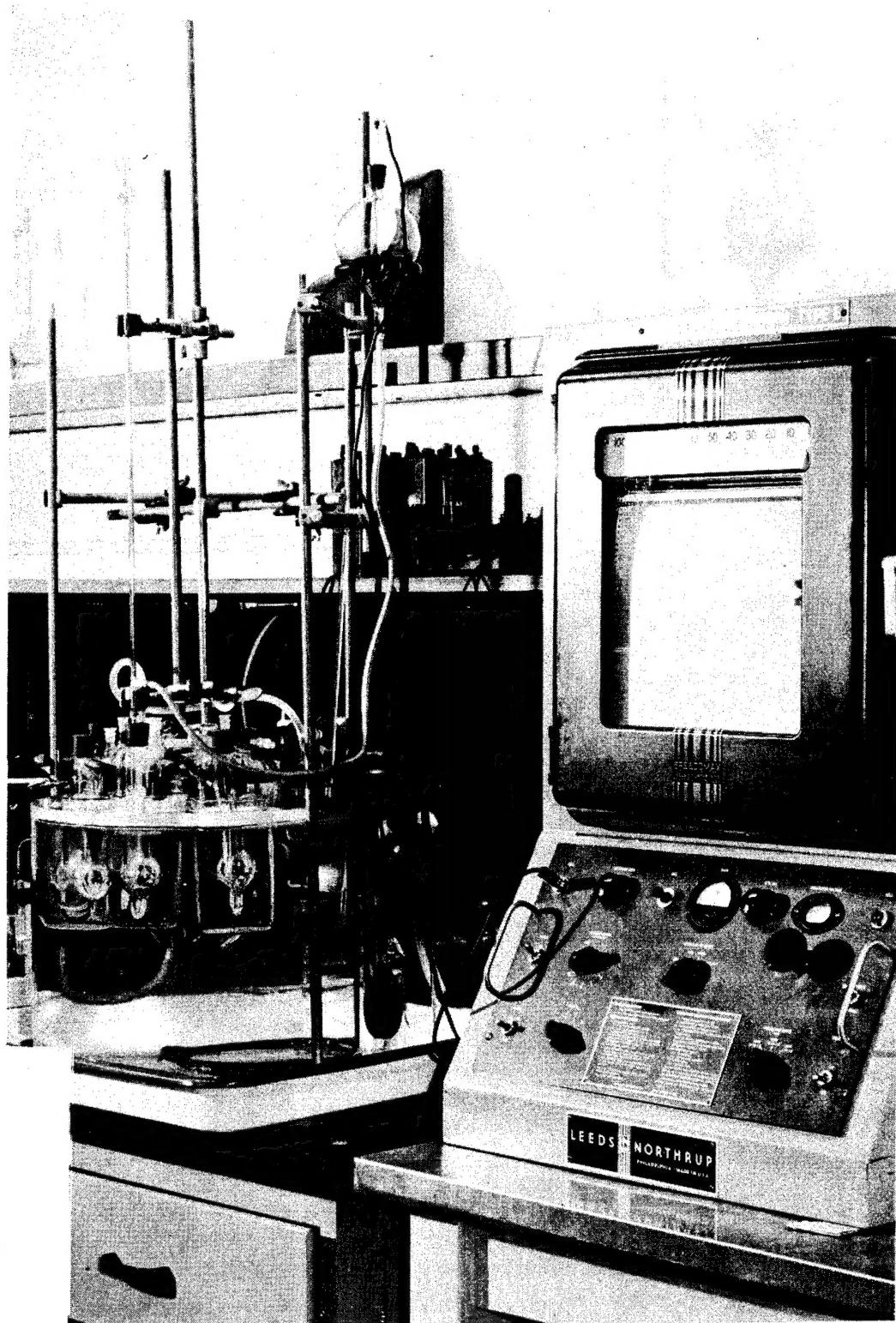


Figure 2

by Schulman, Battey and Jelatis<sup>(4)</sup>. The instrument was found to be quite stable and very satisfactory.

Four cells were used each surrounded by a tall form beaker. These were immersed in a cylindrical thermostat bath (Figure 3). The beakers served to prevent contamination of the water bath in the event of breakage of the cells. The cells were kept at a temperature of  $34 \pm 0.1^\circ \text{ C}$ . This temperature was chosen rather than  $25^\circ \text{ C}$  so that cooling would be unnecessary. The apparatus was kept from vibrating by mounting the entire water bath on sponge rubber. Stirring vibration was minimized by stirring the bath with a small circulating pump connected to the bath by six foot lengths of Tygon tubing. The same capillary and salt bridge were used for each cell. The solutions in the cells were stirred while in contact with a pool of liquid zinc amalgam by bubbling nitrogen gas through them for thirty minutes. The nitrogen was first bubbled through a 1M hydrochloric acid solution contained in a wash bottle immersed in the bath.

The polarographic cells used were designed to hold a volume of one to ten milliliters. A diagram of the cell construction is shown in Figure 4. The inside diameter of the cell (A) is large enough to allow the insertion of the capillary and the KCl-agar bridge. The bridge and the capillary are held by a rubber stopper (B) which fits in the widened mouth of the cell. The bulb (C) is filled with saturated liquid zinc amalgam. The level of the amalgam is adjusted by pressure from a

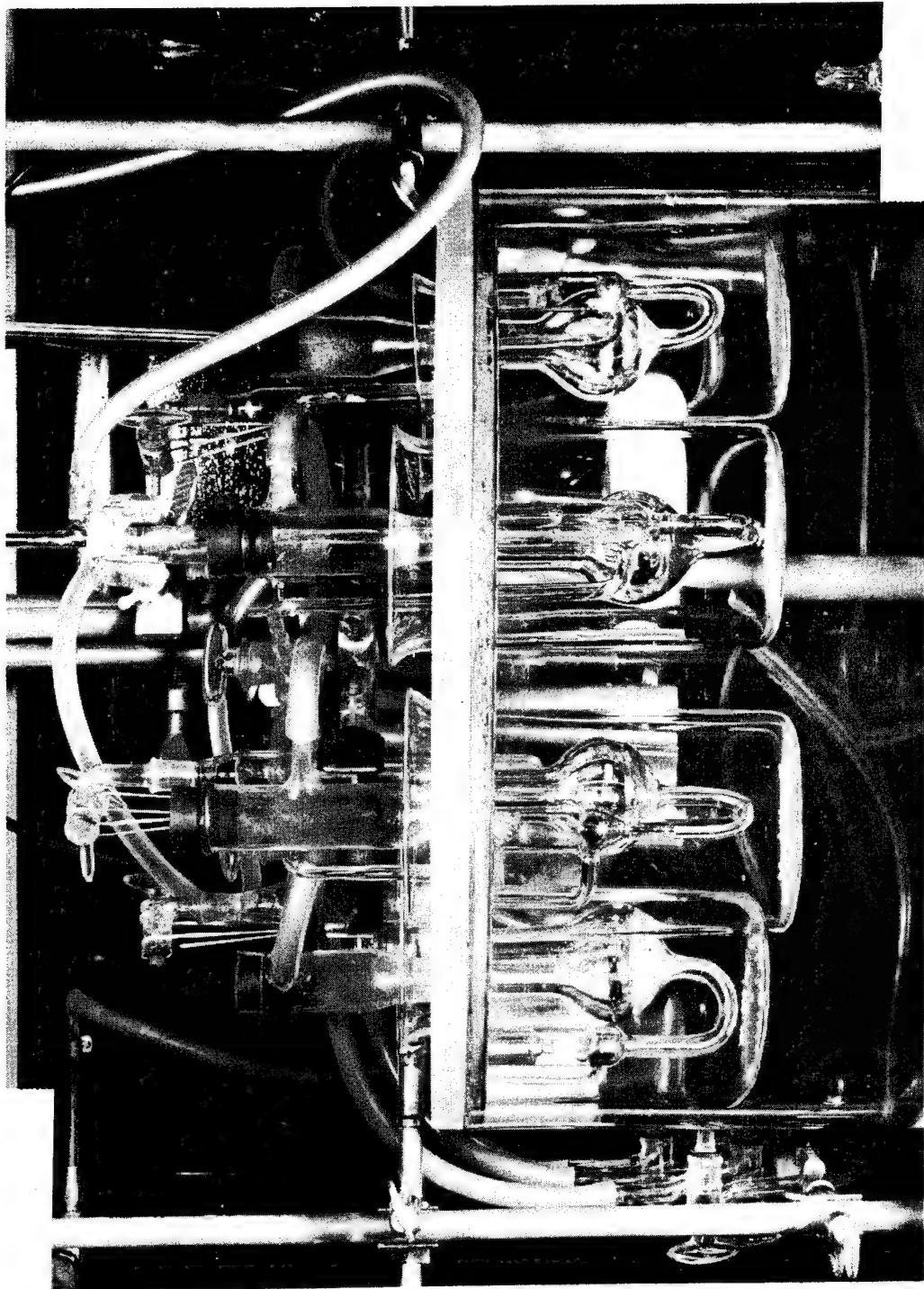


Figure 3

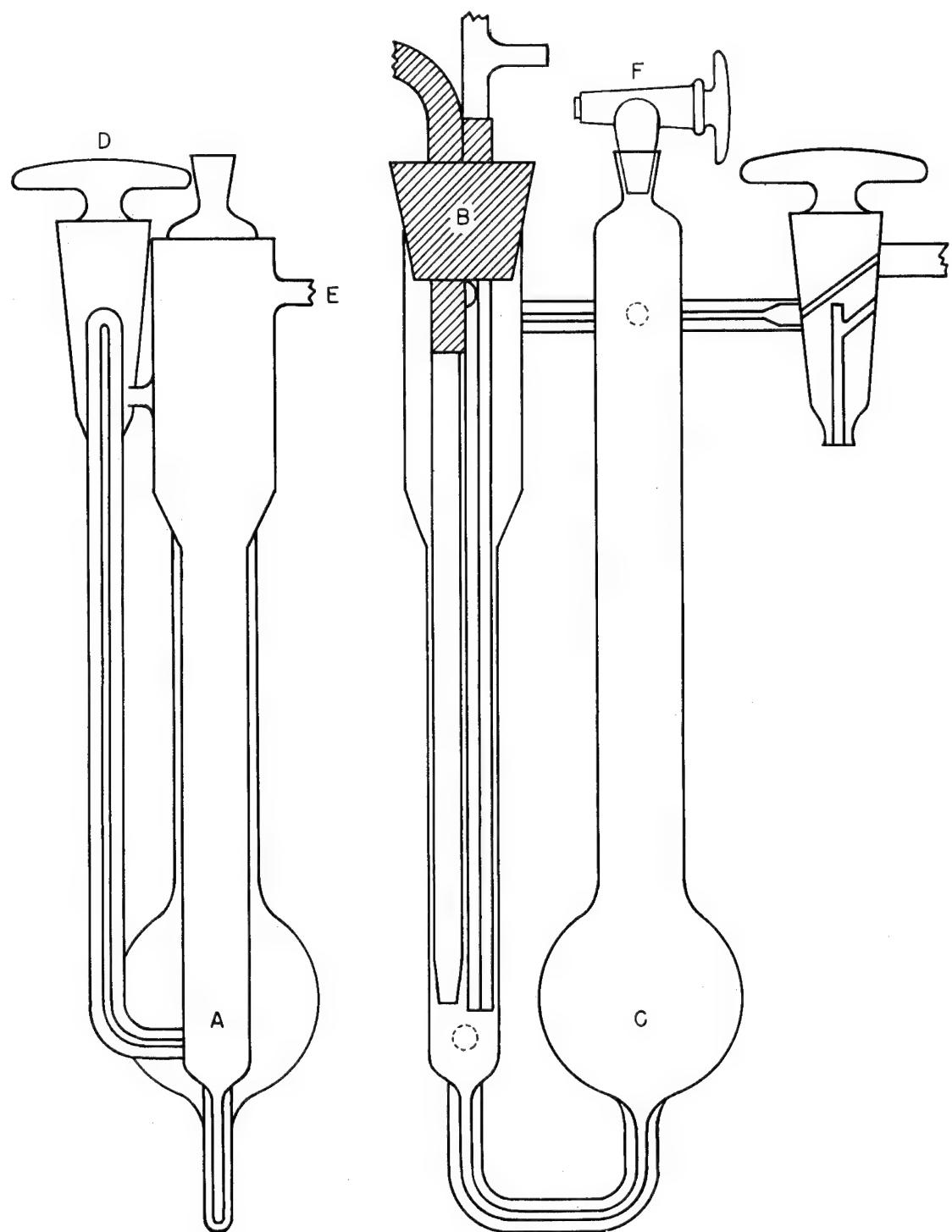


Fig. 4

hypodermic syringe connected to the stopcock (F) which is held firmly in the ground glass joint by means of a rubber band. Nitrogen gas is bubbled through the solution in the cell by opening the three-way stopcock (D). During the deoxygenation process the level of the amalgam in the cell space (A) is so adjusted that the entering gas effectively stirs the solution-amalgam interface. The other stopcock channel allows the cell to be opened to the atmosphere during analysis. The gas outlet (E) is connected to a gas washing bottle of dilute sulfuric acid in order to prevent spray from contaminating the atmosphere. The cells were emptied by inserting in the cell a small Tygon tube connected to a suction bottle and were cleaned by rinsing three times with distilled water and twice with acetone.

The capillary used was a piece of 0.05 mm diameter marine barometer tube 17 cm long. When not in operation it was kept immersed in mercury and frequently cleaned by immersion in concentrated nitric acid. The height of the mercury in the leveling tube was kept constant at 70 cm (measured from the tip of the capillary). The capillary constant was measured frequently and was determined as  $m^{2/3} t^{1/6} = 2.28$  in 1M KCl with shorted electrodes.

The KCl-agar bridge connecting the saturated calomel electrode was of the type recommended by Hume and Harris<sup>(5)</sup>. The probe containing the KCl-agar was a 11.5 cm, 7 mm O.D. glass tube slightly tapered at the end. Readjustment of the agar plug was achieved by applying pressure

with a hypodermic syringe connected to a stopcock inserted in the top of the calomel cell (Figure 5). This bridge was easily replaceable and reproducible.

Apparatus for the preparation of the solutions to be analyzed is shown in Figure 6. Calibrated 5 ml volumetric flasks placed in test tubes and covered by funnels were used for the evaporation of the sample solutions to the sulfate crystals. In case of "bumping" this method offers some chance of recovery. Side holes were made in the test tubes to allow the water vapor to escape. The test tubes placed in a beaker were heated by means of an infra-red lamp. The sulfate crystals were treated in the flasks with granulated zinc and hydrochloric acid and after heating the solutions were cooled to room temperature by immersing the flasks in water using the apparatus shown at the right in Figure 6. The solutions adjusted to the proper volume are transferred to the polarographic cell by means of a 3 ml volumetric pipette equipped with a syringe. All these operations should be carried out in a drybox designed for the handling of plutonium solutions.

#### REAGENTS

##### General

Agar - Braun Corporation, Los Angeles, California

Acids - Bakers Analytical Reagents

Mercury - Distilled

Nitrogen - Tank nitrogen (further purification found unnecessary)

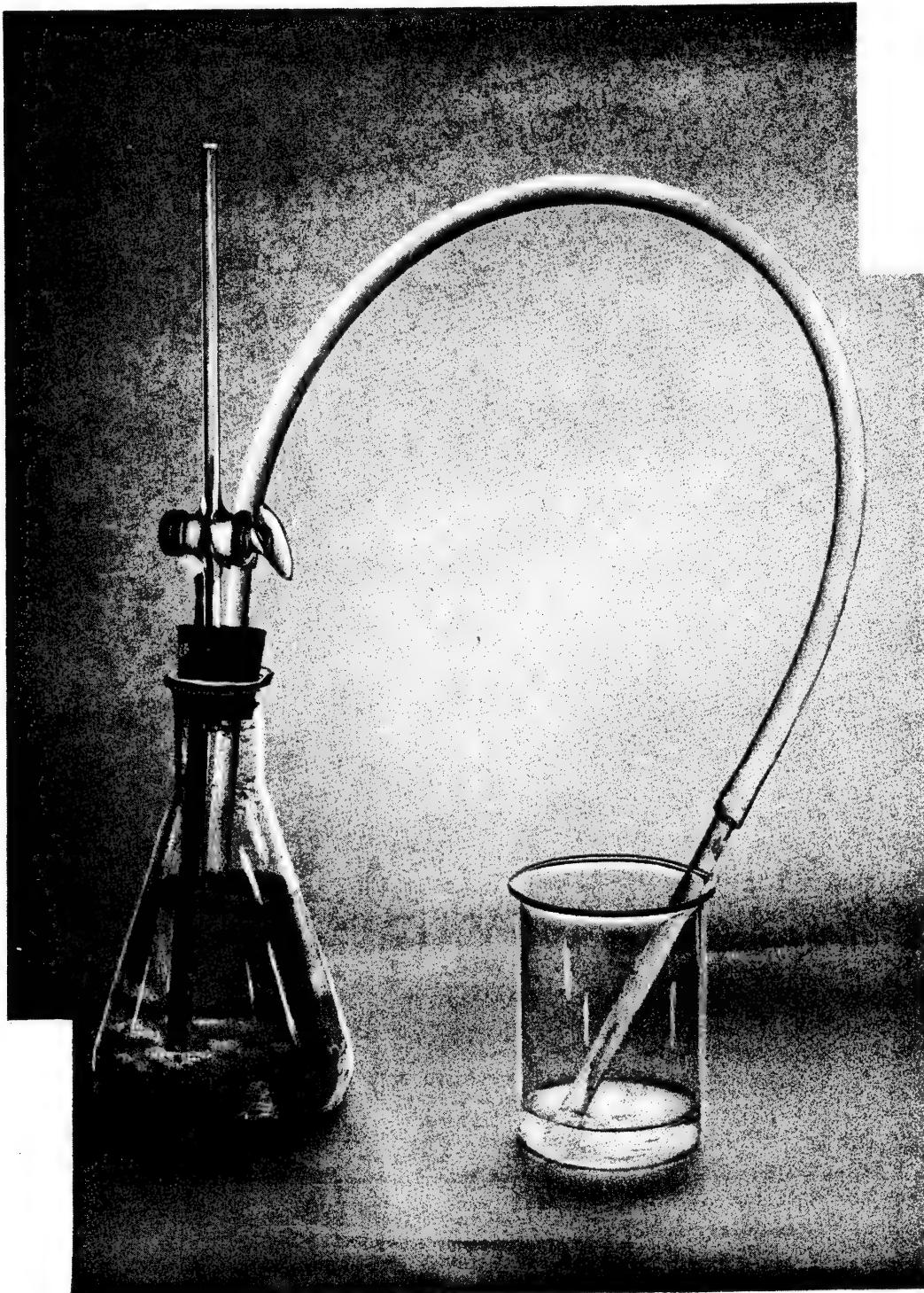


Figure 5

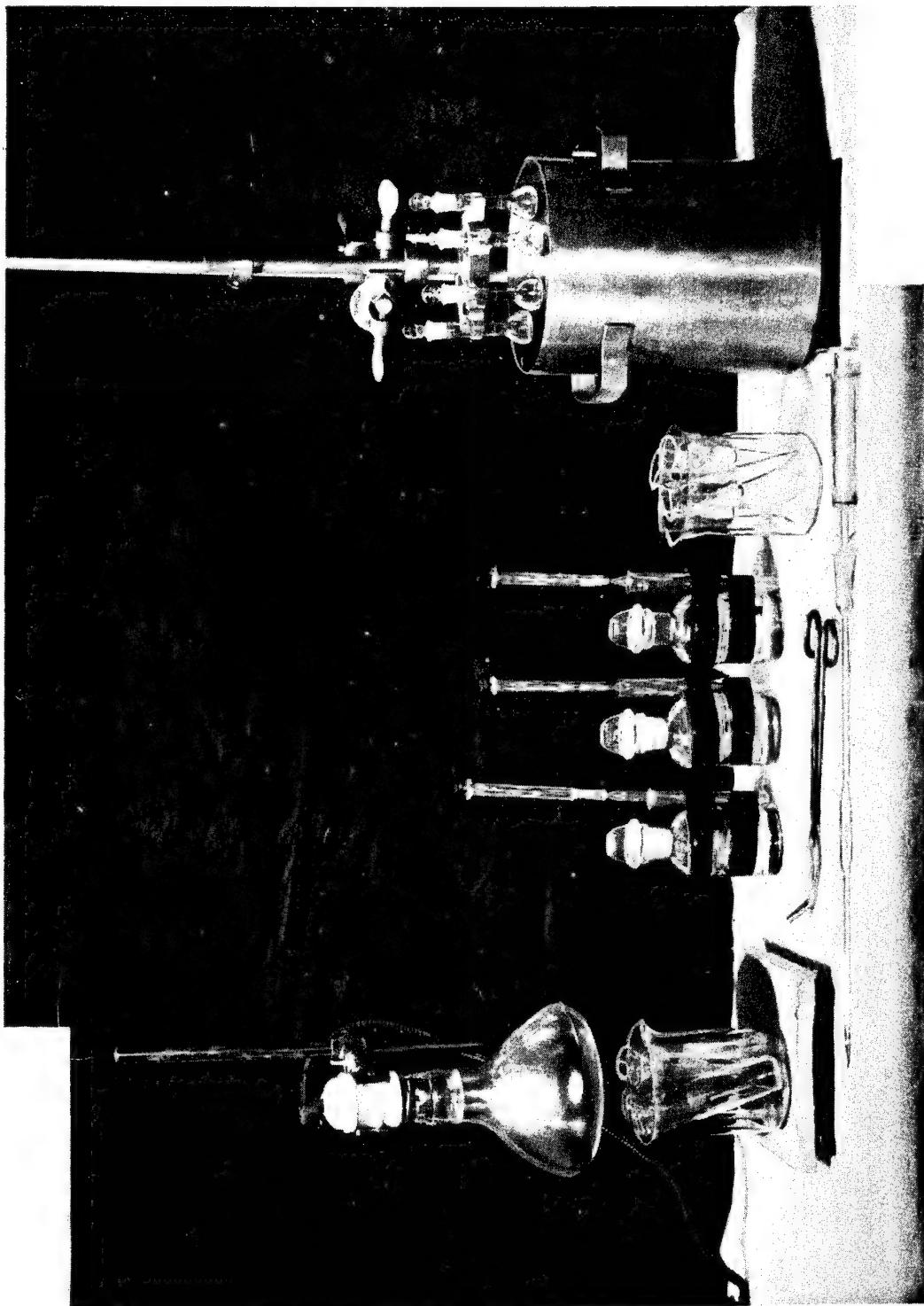


Figure 6

Potassium Chloride, Analytical Reagent - Mallinckrodt Chemical Works

Plutonium - 99.8% pure metal

Vanadium Pentoxide, C.P. - Fisher Scientific Company, Pittsburgh, Penn.

Zinc Metal Dust, Analytical Reagent - Mallinckrodt Chemical Works

Zinc Metal Granular 20 mesh, Analytical Reagent - Mallinckrodt Chemical Works

Special

The liquid zinc amalgam was prepared by adding 2.2% by weight zinc dust to pure mercury and shaking the mixture in a glass stoppered bottle with 0.5M hydrochloric acid solution.

The agar for the agar-KCl bridge was prepared by dissolving 3 grams of agar in 100 ml of distilled water and adding 26.0 grams of KCl.

Fresh distilled water was used in preparing all solutions.

RECOMMENDED PROCEDURE

The following procedure is recommended for the polarographic determination of vanadium in a plutonium-vanadium sample. The method may be used for solid samples such as metal, oxide or fluoride, or for acid solutions. In the case of solid fluoride samples, the sample is converted to the sulfate by heating with strong sulfuric acid and the excess removed by fuming. Oxide samples may be converted to the sulfate by treating the solid samples with hydroiodic acid and the excess hydroiodic acid removed by fuming with sulfuric acid. For samples con-

sisting of sulfuric acid solutions of the metal it is advisable to heat the solutions almost to dryness in order to remove the excess sulfuric acid. The amount of sample taken may be weighed or measured volumetrically depending on the type of sample and on the units in which the vanadium content is to be expressed.

1. Electropolish<sup>(6)</sup> approximately 100 milligrams of the metal alloy sample and weigh accurately in a calibrated 5 ml volumetric flask.
2. First dissolve the sample by adding 0.5 ml of 3M HCl, and then add 0.5 ml 6N H<sub>2</sub>SO<sub>4</sub> and 0.5 ml 8M HNO<sub>3</sub>. Micro pipettes (500  $\mu$ ) equipped with syringe are used for adding the acids.
3. Place the flask containing the sample in a test tube with two side holes near the top and cover the test tube with a small funnel in such a manner that the stem of the funnel is outside the flask.
4. Place the test tube containing the flask and solution in a beaker underneath an infra-red heating lamp, and evaporate to dryness (about 5 hours).
5. Moisten the crystals with distilled water and again evaporate to dryness to remove traces of volatile acids.
6. Add 0.15  $\pm$  0.02 grams of granulated zinc to the flask (making use of the small funnel). Next add exactly 3 ml of 1.67M hydrochloric acid.
7. Place a small glass bulb in the mouth of the flask and heat under the infra-red lamp for approximately thirty-five minutes until the zinc is completely dissolved.

8. Turn off heat, remove bulb from the mouth of the flask and wash off the tip into the flask with approximately one ml of distilled water.
9. Place the flask in a clamp and immerse in water for three minutes.
10. At the end of this time, remove the flask from the water and adjust the volume to the 5 ml mark by adding distilled water from a micro-pipette.
11. Place the stopper in the flask and mix the solution thoroughly by inverting the flask several times.
12. Use a 3 ml pipette fitted with a syringe to transfer 3 ml of the solution to the polarographic cell.
13. Cover the cell with a rubber stopper, turn on the nitrogen and adjust the level of the zinc amalgam in the cell by means of a syringe connected to the stopcock in the cell reservoir. The amalgam should be adjusted so that the entering gas stream effectively stirs the surface interface.
14. Deoxygenate the solution for thirty minutes. (It should be emphasized that slight changes in the volume of the cell solution due to evaporation affect the accuracy, therefore conditions of bubbling the nitrogen through the solution should be kept as constant as possible. This effect is perhaps greater in this procedure since a fairly rapid flow of gas through the cell is necessary to stir the amalgam surface. Possibly a flow meter or a device to insure the passage of the same volume of nitrogen through the cells might help to minimize the source of error due to evaporation.)

ation during the deoxygenation process).

15. During the deoxygenation process immerse the capillary and the salt bridge in a small beaker of 1M hydrochloric acid. Before immersing in the cell solution the electrodes are rinsed with distilled water and dried with "Kleenex" tissue.
16. When the deoxygenation is completed replace the rubber stopper of the cell with the electrode assembly, shut off the nitrogen and open the cell to the atmosphere by turning the three-way stopcock.
17. Lower the level of the amalgam pool by opening the stopcock in the cell reservoir.
18. Adjust the mercury level in the stem tube to the predetermined height and record the drop time with the circuit open. Determine the proper sensitivity range and record a polarogram between -0.2 and -0.8 volts. Record at least two polarograms for each solution.
19. Determine the maximum current in microamperes (measuring from top to the bottom of the anodic wave) at -0.3 and -0.7 volts.

#### CALIBRATION DATA

Four quantities ( $1.4281 \pm 0.0001$  grams each) of dry C.P.  $V_2O_5$  were placed in calibrated 500 ml volumetric flasks and dissolved with hydrochloric acid. The volumes were adjusted to 500 ml by adding distilled water. Nine dilutions were made on each of the four stock solutions to produce nine sets of solutions of different vanadium concentration. These solutions were prepared by pipetting the desired amount of the stock solution into a 50 ml flask and diluting to the

mark with distilled water. The volumes of all the flasks used were checked by adding known volumes of mercury and were estimated to be accurate within 1% of the correct volume. All pipettes were calibrated. The solutions analyzed were picked at random and all thirty-six of the solutions were analyzed. A two ml sample was taken from each of the dilute vanadium solutions and added to a calibrated 5 ml flask containing 100 milligrams of plutonium in the form of a chloride solution. Analyses of these solutions were made according to the method described in the foregoing "Recommended Procedure" starting with the addition of nitric and sulfuric acid (Step (2)).

The results obtained are shown in Table I and the calibration curve is plotted in Figure 7.

Table I  
Relation of the Diffusion Current  
to the Vanadium Concentration

<u>V/Pu</u> <u>(x 10<sup>3</sup>)</u>	<u>Concentration</u> <u>Milligrams V/l</u>	<u>i<sub>d</sub></u> <u>(u.a.)</u>	<u>K</u> <u>(c/i<sub>d</sub>)</u>
1.28	25.60	1.98 ± 0.04	12.93 ± 0.26
2.56	51.20	3.90 ± 0.10	13.13 ± 0.34
4.48	89.60	6.71 ± 0.07	12.97 ± 0.13
6.40	128.00	9.98 ± 0.26	12.83 ± 0.33
9.60	192.00	14.59 ± 0.29	13.16 ± 0.26
12.50	256.0	19.56 ± 0.11	13.09 ± 0.07
16.00	320.0	24.59 ± 0.27	13.01 ± 0.14
19.20	384.0	29.66 ± 0.35	12.95 ± 0.15
22.40	448.0	34.35 ± 0.24	13.03 ± 0.07

Plutonium concentration equals 20.0 milligrams/ml

σ equals Standard Deviation

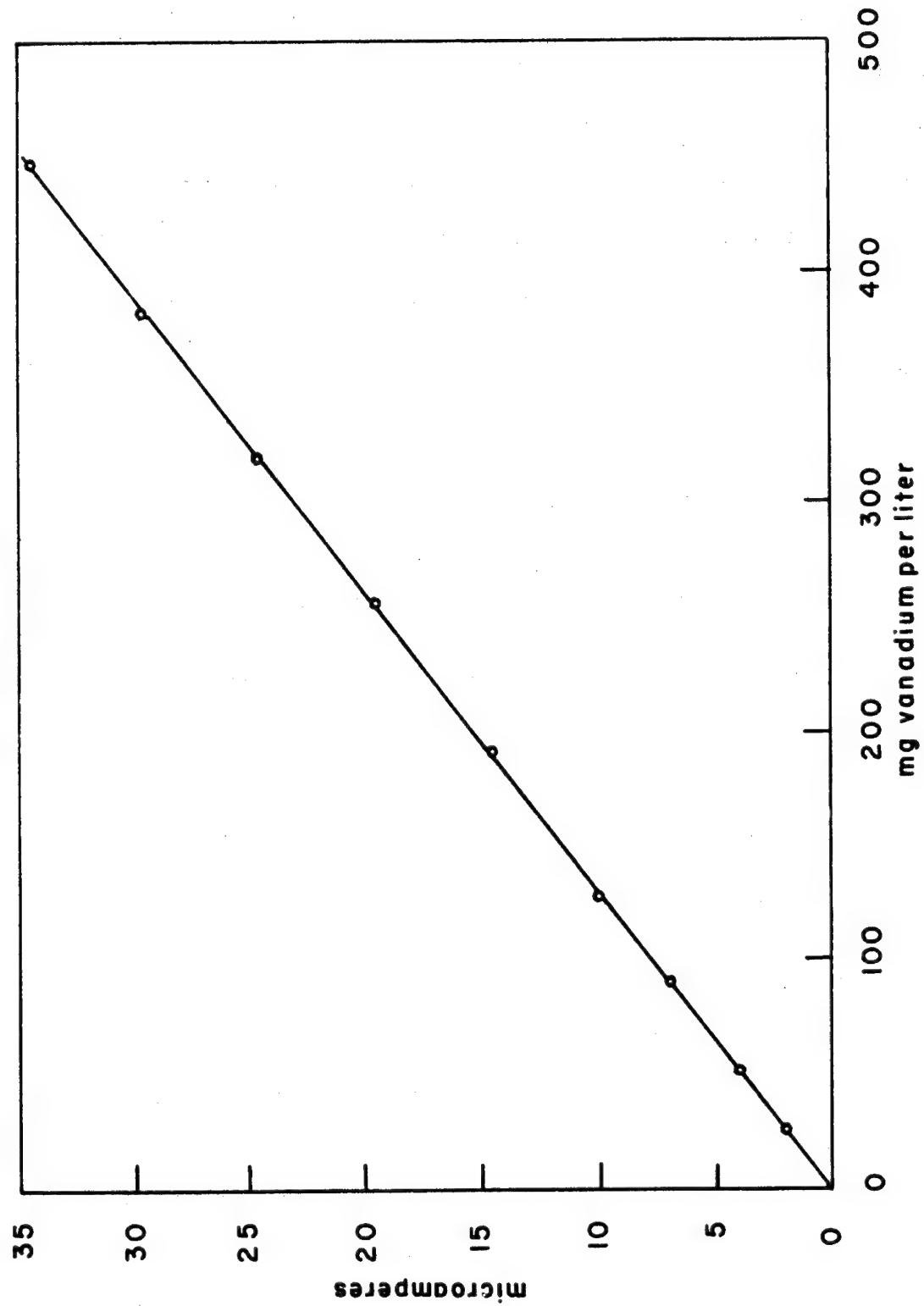


Fig. 7 Calibration Curve

The first column gives the weight ratio of the vanadium to the plutonium. Column three shows the diffusion current in microamperes measured at -0.3 and -0.7 volts. Each value for the diffusion current is the average of eight measurements, two on each of the four separately prepared vanadium-plutonium solutions. The average value for the calibration constant is  $K = 13.01 \pm 0.22$  milligrams  $V/l u.a^{-1}$ .

The effect of the plutonium concentration on the calibration constant ( $K$ ) is shown in Table II.

Table II  
Dependence of Calibration Constant  
on Plutonium Concentration

Sample Size (Milligrams)	Plutonium Conc. Milligrams/ml	K Milligrams $V/l u.a^{-1}$ . $\sigma$
200	40	$13.22 \pm 0.08$
100	20	$13.01 \pm 0.22$
50	10	$13.17 \pm 0.14$
10	2	$13.13 \pm 0.24$

$\sigma$  equals Standard Deviation

Four solutions, two containing  $5.12 \times 10^{-2}$  mg  $V/ml$  and two containing  $25.6 \times 10^{-2}$  mg  $V/ml$  were analyzed for each plutonium concentration. The calibration constant ( $K$ ) shown in the third column was calculated by dividing the concentration of vanadium in milligrams/liter by the measured diffusion current in microamperes. Considering the data in Table II and the experimental error (about 4%) there is no dependence of the calibration constant on the plutonium concentration within this

range (40 milligrams Pu/ml to 2 milligrams Pu/ml). A plutonium sample size of 200 milligrams is approximately the largest size feasible for this method. Larger samples (300 milligrams) did not completely dissolve under the conditions defined by the experimental procedure. Since 100 milligram plutonium samples were used in determining the relation of the diffusion current to the vanadium concentration (Table I), and since the data given in Table II shows that the calibration constant is independent of the plutonium concentration, the use of a 200 milligram sample would extend the lower limit of the vanadium analysis to solutions with a  $V/Pu$  ratio of  $6.4 \times 10^{-4}$ .

#### PRECISION

Based on the data shown in Table I the confidence limits for the range  $V/Pu = 1.28 \times 10^{-3}$  to  $V/Pu = 22.4 \times 10^{-3}$  are 3.4% for the 95% confidence level and 4.5% for the 99% confidence level. These figures are based on seventy-one degrees of freedom (two measurements on thirty-six separate analyses).

#### CALCULATIONS

The percent vanadium in an alloy may be calculated according to the general formula

$$\% V = \frac{0.5 K (i_d)}{\text{wt. of sample in milligrams}}$$

where  $K$  is the calibration constant in milligrams  $V/1 \text{ u.a}^{-1}$ . and  $(i_d)$  is the measured diffusion current. Under the conditions used (Temperatures =  $34.0 \pm 0.1^\circ \text{ C}$  and  $m^{2/3} t^{1/6} = 2.28$ ) the formula becomes

$$\% V = \frac{6.51 (i_d)}{\text{wt. of sample in milligrams}}$$

### INTERFERENCES

Since the sample is converted to the sulfate by fuming with sulfuric acid, nitrate and halide ions are removed. In cases where organic anions are present it is advisable to remove them by fuming with nitric and perchloric acid before the final conversion to the sulfate.

Of the metallic ions data were obtained only on those expected to be present in samples to be analyzed. Table III shows the effect on the calibration constant of samples containing 0.1% of the materials listed in the first column.

Table III  
Effect on the Calibration Constant Due  
to the Presence of 0.1% of Various Metals

Metal	K	$\sigma$
Iron	13.23	$\pm 0.19$
Cobalt	13.32	$\pm 0.22$
Manganese	13.40	$\pm 0.15$
Nickel	13.46	$\pm 0.16$
Chromium	12.99	$\pm 0.11$

$\sigma$  equals Standard Deviation

Four solutions of each metal, two containing  $8.96 \times 10^{-2}$  milligrams V/ml and two containing  $25.6 \times 10^{-2}$  milligrams V/ml were analyzed. All the metal solutions contained 20 milligrams/ml of plutonium. Since the change in the calibration constant,  $K = 13.01 \pm 0.22$  milligrams V/l u.a<sup>-1</sup>., is less than the experimental error in all cases, it is

evident that the metals in Table III do not appreciably interfere in the analysis. It should be mentioned however, that two of the sample solutions containing 0.1% chromium could not be readily reduced by the zinc evidently due to the formation of a coating on the granule surface which prevented the zinc from dissolving. Possibly this could be avoided by reversing the order in Step 6 of the "Recommended Procedure", that is, adding the hydrochloric acid before the zinc.

As mentioned before uranium interferes by producing an anodic wave.

#### SUMMARY

It is possible to analyze for vanadium polarographically in the presence of plutonium by first reducing the hydrochloric acid solution of the metals with zinc and zinc amalgam. Plutonium solutions with vanadium-plutonium ratios of  $6.4 \times 10^{-4}$  to  $22.4 \times 10^{-3}$  may be analyzed with a reproducibility of about 4%.

The following constituents present in amounts as much as 0.1% were found not to interfere with the analysis: iron, cobalt, nickel, manganese and chromium.

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